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Analysis of activation energies and decay-time constants of potential-induced degraded crystalline silicon solar cells

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Abstract

A laboratory type PID-test system was used to measure degradation curves of the shunt resistance during the stress test. It was found that these curves feature typically an initial plateau without significant changes and a mono-exponential decay, both having temperature depended time constants: The plateau length as well as the decay time constant behave Arrhenius-like. Performing these degradation measurements under various temperatures enable the identification of PID relevant activation energies. A solar module compound made of industrial-type crystalline silicon solar cells was investigated and an activation energy of the decay was determined to $(0,95 \pm 0,14)$ eV.

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1. Introduction

Potential induced degradation by the shunting type (PIDs, further referred to as PID) of crystalline silicon solar cells is still a not fully described phenomenon. The effect can be reduced or even avoided on cell level, module level or system level. Many manufacturers have decided to produce already PID free solar cells. To check the PID resistance of a certain solar cell architecture a supplement of an already existing quick PID test procedure [1] is suggested. This PID test on cell level measures the reverse characteristic parallel resistance R_{shunt} and gives a good

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correlation to PID in the module and system level [2]. Although this type of PID testing was introduced to the community several years ago, so far no activation energy measurements were done using it. Nevertheless, activation energy measurements were published so far by Raykov et al. [3], Taubitz et al. [4] and Hacke et al. [5] for temperature dependent leakage current measurements in solar modules. These values are in the range of 0,4 eV/0,7 eV [3], 0,73 eV [4] and 0,86 eV [5].

The complex system of materials and interactions makes it very difficult, to give a physical interpretation of the origin of this activation energy. So far it is commonly accepted, that the PID effect is correlated with

- the composition of anti reflection coating made of silicon nitride and the interfacial properties to the silicon surface underneath [6,7], and
- sodium occurrence in silicon: Stacking faults are decorated with a huge amount of sodium [8].

In this contribution the temperature dependent analysis of solar cell R_{shunt} degradation curves is developed and applied to measure the activation energy E_A of the degradation mechanisms to give access to an important measure related to PID.

2. Experimental

Industrial type crystalline silicon solar cells were fabricated using 3-6 Ohmcm Cz-wafers. The process sequence is based on industrial features, having an alkaline texture, a phosphorus diffusion, a PECVD SiN_x -Antireflection Coating (ARC) and screen printed metallization based on silver on the front and aluminum on the rear. A certain type of solar cell was used in the experiments, which were known to be PID-prone. Such solar cells were locally degraded in a laboratory apparatus as pictured in Fig. 1: On the front side of the cells a stack of EVA and a TCO coated glass were mounted (TCO on the upper side). To investigate the cells, the EVA foil used must be PID prone, hence not to suppress PID. This stack was placed onto aluminum foil and further on a precision hot plate. Between the front-glass TCO and the solar cell base, a high voltage of 1000 V was applied, the minus polarity on the cell base contact. This high voltage can cause a potential induced degradation to the solar cell. Since not all the solar cell area was covered with EVA and glass, the front contacts of the solar cell were partly free. The high voltage stress was applied for several temperatures between 54 and 82 degree Celsius ($^{\circ}\text{C}$). During the degradation, the shunting resistance of the solar cell was measured by applying a low reverse voltage of 100 mV and measuring the corresponding current (see Fig. 1 a). The PID stress was applied for several hours until a significant R_{shunt} degradation was observed. The cells were characterized prior to and after the PID-stress test by means of light IV (under STC), electroluminescence (EL) and Dark Lock-In Thermography (DLiT). Such measurement results were shown in Fig. 1 b) as an example indicating the typical PIDs related degradation phenomena: Reduction of parallel resistance R_{shunt} followed by a decrease in fill factor FF , efficiency η and later open circuit voltage V_{OC} . In the EL

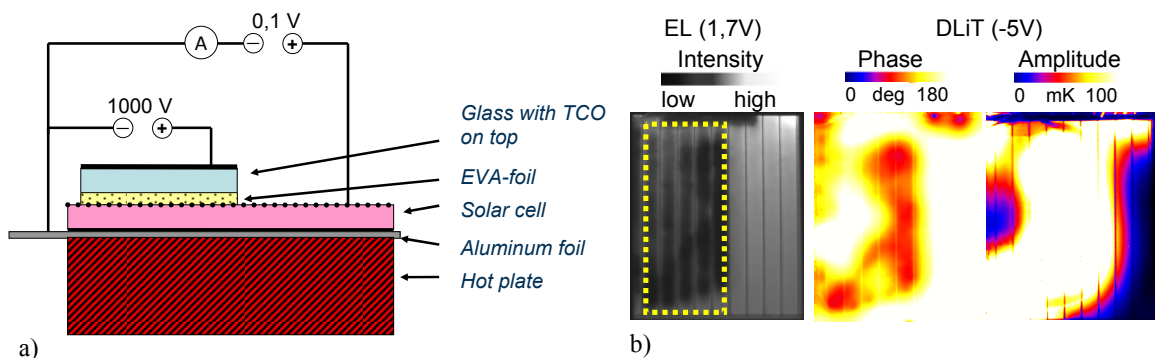


Fig. 1. Simplified cross section of experimental setup (a). Representative EL and DLiT pictures of a PID-affected solar cell after PID-degradation are shown in (b). PID occurs in area of the solar cell which was covered by the EVA and glass (yellow frame in EL). Sample sizes are 20x25 mm², PID-area ~10x20 mm².

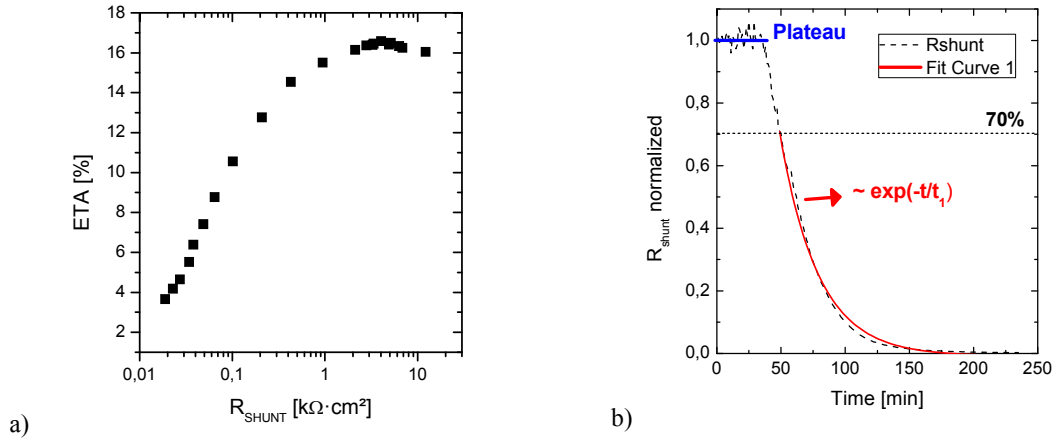


Fig 2. Clear correlation between R_{shunt} and light IV efficiency η_{IV} (a) The normalized R_{shunt} curves obtained feature a plateau, an abrupt decay (showing sometimes nonuniformities), and the part with a steady behaviour (<70% of initial values), which was used to fit the mono-exponential decay (highlighted in red).

picture dark areas appear, on the same sites the lock-in pictures of phase and amplitude indicate shunts. The clear correlation of the measured R_{shunt} values to the efficiency is shown in Fig. 2 a): To measure this curve, a PID test of a solar cell was done and cell was removed from the PID-test regularly to perform IV-measurements under STC. As long as the R_{shunt} value exceeds a value of about 3 kΩcm² there is no impact to the efficiency. For smaller R_{shunt} -values the efficiency is clearly correlated.

The R_{shunt} -degradation curves were measured automatically with a high resolution of one data point per minute (Fig. 2 b). The curves obtained were normalized to the plateau values, resulting in normalized values to unity. Two parts of those degradation curves were analysed: First, the steady state plateau at the beginning of each degradation process indicated by the plateau duration τ . Second, this plateau is followed by a steady decrease: Assuming any kind of concentration change is responsible for the R_{shunt} -degradation, a mono-exponential decay of the type

$$R_{shunt} = A_1 \cdot \exp\left(-\frac{t}{t_1}\right) + y_0 \quad (1)$$

can be fitted. This provides access to the specific decay time t_1 . The other fitting quantities A_1 and y_0 were not further used for calculations. The activation energy E_A was calculated using the Arrhenius plot

$$R_{gen} = \frac{1}{\tau_{gen}} = \kappa_0 \exp\left(\frac{-E_A}{k_B T}\right) \quad (2)$$

In this formula, k_B is the Boltzman constant, T the absolute temperature and κ_0 a prefactor (known as frequency factor in collision theory). In this formula τ_{gen} was substituted by τ (plateau length) or t_1 (decay time constant), then the Arrhenius line was plotted and fitted. This can be done assuming the process investigated corresponds to a reaction rate, what certainly is true for the decay part of the degradation. We also found a temperature dependence for the plateau length τ , hence we suggest to correlate this measure to a reaction rate, too. Unfortunately, there is a lack of experimental evidence for this assumption.

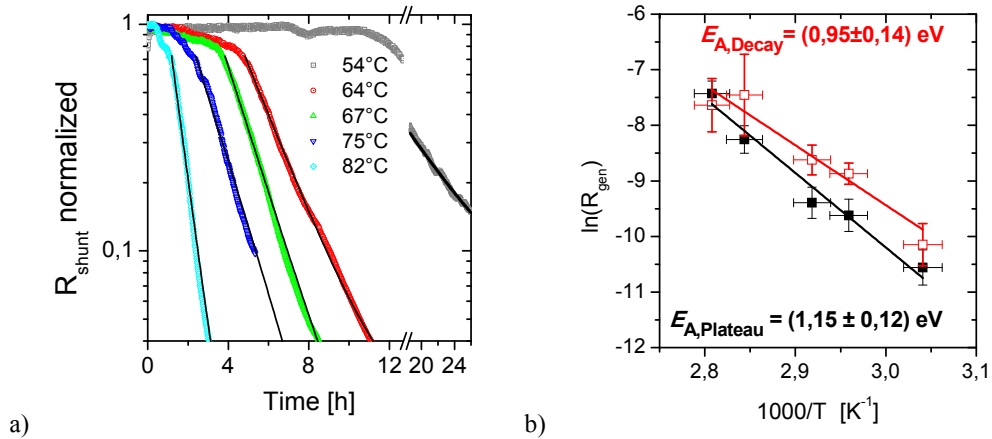


Fig. 3. Shunt-degradation curves obtained at different temperatures (a). In (b) the Arrhenius plots for plateau duration τ as well as the decay t_1 are shown.

3. Results

The measured R_{shunt} -degradation curves are shown in Fig. 3 a) for five different temperatures. Initially the R_{shunt} values of all cells were much higher than $10 \text{ k}\Omega \cdot \text{cm}^2$. As the selected solar cells and the EVA encapsulation foil were known to be PID-prone, typical degradation curves were obtained for all temperatures, even the 54°C -curve degrades to R_{shunt} -values of $<5\%$ of the initial value (not shown in the graph). All curves feature a mostly clear cognizable plateau, as well as the mono-exponential decay.

The initial plateaus were analysed in terms of the time duration, until the abrupt decrease (minor changes to 80% of the initial values were assumed to belong to the stable plateau). This plateau duration τ is significantly depending on the temperature. In Fig. 3 b) the τ values of the different temperatures were used in combination with (2) for the Arrhenius plot and the activation energies $E_{A,Plateau}$ were calculated. The error bars in x and y direction were calculated using the statistical failure of the temperature measurements (0,7%) and the assumed failure in the manual determination of the plateau length (1%). The activation energy obtained from these calculations $E_{A,Plateau}$ $(1,15 \pm 0,12) \text{ eV}$.

R_{shunt} decay curves starting from values less than 70% of the initial values were used to calculate the temperature-specific decay times t_1 . This 70%-edge was introduced because of uncertainties which may occur. In combination with formula (2) the Arrhenius plot was examined and the activation energies calculated, which is also shown in Fig. 3 b). From the linear fit of these data points, the activation energy for the R_{shunt} -decay $E_{A,Decay}$ was determined to be $(0,95 \pm 0,14) \text{ eV}$.

4. Discussion

All the R_{shunt} degradation curves feature an initial plateau at which no significant change of the R_{shunt} values occurs, the measurements vary in the range of the uncertainty or show only minor decrease. During this time, no degradation in the efficiency can be recognized (see Fig. 2 a). Then, the plateau stops abruptly and a mono-exponential decay follows, typically to low R_{shunt} values of less than 5 % of the initial value, which means values of some hundreds $\text{m}\Omega \cdot \text{cm}^2$. In most cases the degradation has been stopped, before the R_{shunt} value has saturated.

The activation energies of 0,95 eV and 1,15 eV were calculated for the decay and initial plateau length, respectively. As initially discussed in section 2, the decay time t_1 fulfil the requirements of the Arrhenius specification, they are correlated to a reaction rate. In contrast, the physical origin of the plateau length is not fully understood so far. Even though, the nice temperature dependence suggests a reaction rate τ may also depend on the

reaction rate which is correlated with the R_{shunt} -decay. Either by a set of samples having particularly difference in the architecture or by dedicated material/impurity analysis conclusions on the origin of the plateau length may be drawn.

Nevertheless, the decay measurements show nicely, that the method is well suited to calculate activation energies of PID prone solar module compounds. The uncertainties are acceptable and could be decreased, e.g. by a better heating control.

Other published values for E_A range from 0,4 eV [3] to 0,86 eV [5] for PID on module level. In these papers the leakage current between the inner solar cells and the module frame was analysed. Compared to our experiments, additional different solar cells were used, too. Nevertheless, it can be assumed that, the degradation mechanism of PID is the same for all, since the obvious measurements (IV performance, EL and DLiT) show a similar behaviour.

Due to the large differences between all the reported E_A values from the literature and our contribution, it is suggested that, the defect kinetics are depending from the cell and module architecture. Potentially PID should not easily be addressed to only one certain physical behaviour, PID is much more a very complex procedure, taking into account the EVA foil and the ARC used. Nevertheless, all PID prone solar material combinations feature the same final status: The partly or even fully degradation of solar cell performance by means of internal shunting, whereas in the shunted regions sodium is detectable, which may be the reason for the shunting [5,8]. Since the sodium is not detectable prior to PID, obviously the sodium is introduced into the silicon by the external field. The origin of the sodium and the trace of the sodium from its source to the silicon are responsible for the differences in PID-degradation behaviour of different solar cell architectures, resulting in this wide range of activation energies.

The highly interesting question is: To which physical process is this activation energy E_A correlated? Assuming again the probable scenario that, sodium is the relevant species which is responsible for the PID effect, in this case sodium is initially available only in the encapsulation material “outside” the solar cell. Then sodium must move 1) through the silicon nitride antireflection layer, 2) through a possibly available interfacial layer and the 3) into the silicon. From the theory it is known that, the formation energies of the sodium diffusion in silicon stacking faults ranges from 0,3 to 2,3 eV [9]. Our measurement is in the window of values from theory and corresponds in the range of the failure to the literature. For a detailed analysis of the shunting kinetics solar cells with different architectures should be investigated by means of such a PID test system and activation energy measurements.

5. Conclusion

Successfully a PID-tests setup was used to measure the temperature dependence of the PID-effect of a certain PID-prone module compound made of PID-prone solar cells and PID-prone EVA foil. The measurements approve such a setup to check not only the PID-resistance of solar cells or encapsulation materials but give also access to determine the PID kinetics in terms of time decay constants and activation energies.

For the investigated module compounds PID tests were performed at different temperatures. All the R_{shunt} degradation curves feature an initial plateau at which no significant change of the R_{shunt} values occurs, which in parallel reveals no degradation in the efficiency. Then, the plateau suddenly stops and a mono-exponential decay follows, typically to low R_{shunt} values of less than 5 % of the initial value. In this case, the efficiency is clearly limited by the shunting mechanism due the potential induced degradation (PIDs). For these features activation energies were obtained of $E_{A,\text{Plateau}} = 0,95$ eV and $E_{A,\text{Decay}} 1,15$ eV, for the length of the initial plateau and the decay, respectively. Even though, the initial physical origin of the initial plateau is not clear so far, it is possible to address the R_{shunt} -decay to the PID relevant kinetics.

It can be assumed that, these values are depending on the cell architecture and the encapsulation material used. Hence, following papers of our group will address the role of the anti reflection coating, the interfacial layer between the silicon nitride and silicon as well as the role of sodium itself.

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